



Electrochemical reduction of dichlorodifluoromethane on silver and lead electrodes

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Abstract

The electrochemical conversion of dichlorodifluoromethane (CFC-12) was studied on silver and lead electrodes. The main products detected were CHClF_2 , CH_2F_2 , CH_3F and CH_4 . Cyclic voltammetry and constant potential electrolytic experiments in acetonitrile showed that on silver the reduction mechanism starts with the elimination of one chloride ion at -1.05 V. The current density and the product distribution strongly depend on the nature of the electrolyte used. Higher current densities were observed in methanol and acetonitrile, whereas in propylene carbonate (PC) the current density was found to be 13 times lower than that in acetonitrile. This difference was mainly attributed to the differing diffusion coefficient of CFC-12 in various solvents. A consecutive reaction mechanism was proposed to explain the experimental results.

1. Introduction

Chlorofluorocarbons (CFCs) have long been used as refrigerants, solvents and gas propellants. Since they contain chlorine and no hydrogen, they are very stable and do not react with water. In addition they are not toxic and flammable [1]. Nevertheless, they are responsible for ozone depletion, since they release chlorine atoms, which destroy ozone through photochemical reactions [2].

This led to the replacement of the CFC family compounds with refrigerants with hydrogenated CFCs (HCFCs) or even compounds with no chlorine atoms in their molecule (HFCs). HCFCs do not destroy ozone to such an extent, whereas HFCs are totally harmless [3]. Today large amounts of CFCs are stored in refrigeration systems [4] and there is need to transform them to other useful compounds or render them harmless. Thus, it is of interest to investigate the transformation of CFCs to HCFCs or to HFCs.

Efforts have been made recently using electrochemical reduction of CFCs either in organic solvents, such as methanol [4, 5] and acetonitrile [6] or in aqueous solutions using cells with a solid polymer electrolyte [7, 8]. The experimental results showed that the reduction products and their percentage distribution depend on the cathodic potential [6–8], the electrode material [4, 8], of the supporting electrolyte cation and the pH in the case of aqueous solutions [8]. Although the reduction of halogen containing compounds was studied on various metallic electrodes with different

voltammetric techniques, no reference appears concerning the reduction of CFC-12 on silver, which was found to be the most effective electrocatalyst for this purpose in both aqueous [7, 8] and acetonitrile solutions [6]. In addition electrolytic experiments were carried out to study the effect of the concentration of the supporting electrolyte and the nature of the solvent on the reduction of CFC-12. In previous papers [7, 8], from the shape of the curves of product selectivity vs potential, it was shown that the reduction in aqueous solution follows a consecutive reaction mechanism. In this work the same procedure was followed in acetonitrile, which is an aprotic solvent.

2. Experimental details

The experiments were carried out in a three-compartment glass cell equipped with a saturated calomel electrode (SCE) as reference. The reference electrode was connected to the cell via a Luggin capillary at 0.1 cm distance from the working electrode. The working compartment held approximately 30 cm^3 solution and was separated from the other compartments by a fine porosity glass frit. A platinum foil $2 \times 2\text{ cm}^2$ was used as a counter electrode. The cathodes used in the experiments were foils Ag (99.9%, Aldrich) and Pb (99.9%, Merck) having a geometrical area of 0.2 cm^2 . Before each experiment the electrode was polished with alumina and then rinsed with distilled water and consequently with the electrolyte several times. The

solvents used in the experiments were supplied by Aldrich. The electrolysis time in all experiments was 3 h.

The cell and other glassware used were cleaned before each experiment by soaking in a dilute solution of KMnO_4 in concentrated sulfuric acid. The products, in the constant potential electrolysis experiments, were withdrawn from the cell by a flowing stream of CFC-12 with a constant flow rate of 20 ml min^{-1} . This gas stream stirred also the solution. Gas samples from the exit of the cell were taken with a six-way valve and analysed by gas chromatography using a Porapak QS 4 m column at 120°C and a flame ionisation detector [6].

Estimation of the current efficiency of each of the products was made by dividing the measured concentration in the gas stream by the theoretical concentration, assuming all the current was used for the formation of this particular product. The calculations were performed assuming two electrons for CHClF_2 , four for CH_2F_2 , six for CH_3F and eight for CH_4 .

The cyclic voltammetric set-up included a Bank Elektronik Wenking Potentiostan POS 73 and a Linseis LY 1400 x - y recorder. In the cyclic voltammetry experiments the solution was degassed with Ar before the start of each experiment. Then the desired gas was bubbled through the solution for 15 min and during the experiment it was passed over the solution. An Ar stream was passed over the solution in the case of CH_2Cl_2 .

3. Results

3.1. Cyclic voltammetry in acetonitrile

Figure 1 shows the cyclic voltammogram of CFC-12 on an Ag electrode in acetonitrile solution, with supporting electrolyte Bu_4NClO_4 0.1 M. During the anodic sweep

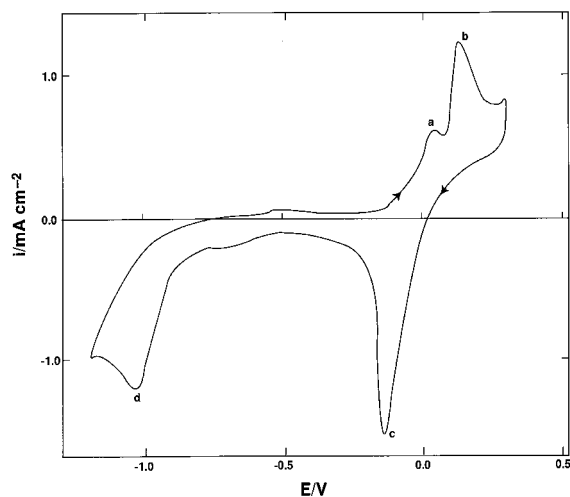


Fig. 1. Cyclic voltammogram of CFC-12 in Bu_4NClO_4 0.1 M on Ag electrode in acetonitrile. Scan rate 100 mV s^{-1} .

two waves appear, first at 0.05 V (a) followed by another at 0.15 V (b). During the cathodic sweep two waves at -0.10 V (c) and -1.05 V (d) are seen. Peak c is strongly dependent on peak b. In addition, the waves b and c were found to be diffusion-controlled, since their i_p is directly proportional to $u^{1/2}$. Moreover, Tafel plots taken at the foot of the wave at -1.05 V , under steady state conditions, showed an approximately one-electron reaction. In Figure 2 the cyclic voltammogram of CFC-12 is shown, with a start potential of -0.50 V . No wave appears during the anodic sweep. This implies that the peaks (a) and (b) are dependent on the electrochemical reactions taking place during the cathodic sweep. On the other hand, if the start potential is at -0.50 V , the wave at -1.05 V always appears and the voltammogram is identical to that of Figure 1. Moreover, when chloride ions were added to the solution, as LiCl , a gradual increase in peak current b and c was observed. Thus, peaks (b) and (c) can be assigned to the couple Cl^-/Cl_2 . The voltammogram showed good reproducibility upon repetitive cycling and this implies that no blocking of the electrode occurs.

To elucidate the role of the fluorine atoms, the electrochemical behaviour of CH_2Cl_2 was investigated. The cyclic voltammogram of CH_2Cl_2 (Figure 3) shows an almost identical form to that for CFC-12. In fact, there is a shift of 0.25 V (of peak d) to more negative potentials. A potential shift was also observed by Wawzonek and Duty [9] during the reduction of these compounds at a mercury electrode. This was attributed to the higher polarity of the C-Cl bond in CF_2Cl_2 than that in CH_2Cl_2 . These voltammetric experiments show

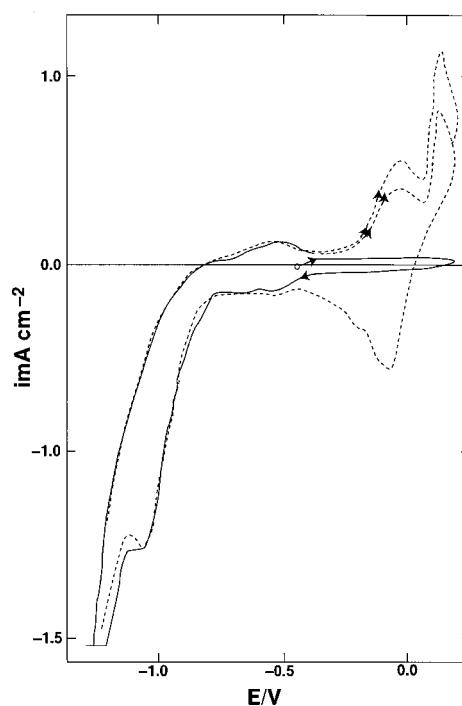


Fig. 2. Cyclic voltammogram of CFC-12 in Bu_4NClO_4 0.1 M on Ag electrode in acetonitrile. Start potential -0.50 V . Scan rate 100 mV s^{-1} .

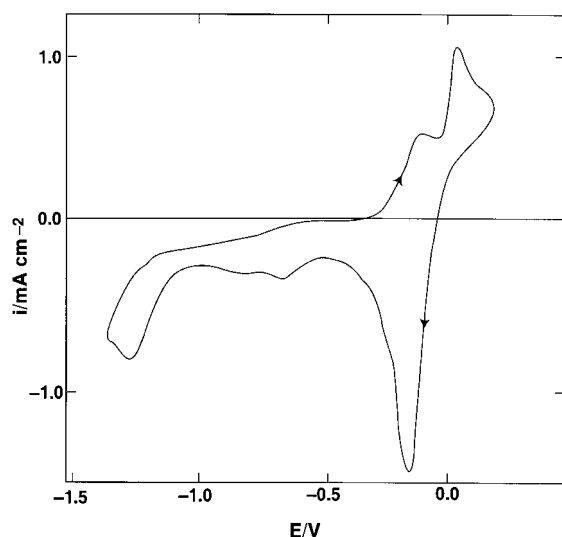


Fig. 3. Cyclic voltammogram of CH_2Cl_2 in Bu_4NClO_4 0.1 M on Ag electrode in acetonitrile. Scan rate 100 mV s^{-1} .

that the fluorine atoms are not involved in electrode reactions at negative potentials up to -1.05 V . It may be concluded that at potential values less than -1.05 V , the elimination of one chlorine atom takes place, which is in agreement with other studies on the reduction of halogen compounds [6, 9–12].

Figure 4 shows the voltammogram on Pb. One broad anodic peak at -0.40 V and two cathodic peaks at -0.60 and -1.00 V , are evident. The peak at -0.95 V is shifted by about 100 mV less negatively compared with the corresponding one for the silver.

3.2. Steady state electrolytic experiments

3.2.1. Influence of the nature of electrode and cathodic potential

The study of the reduction with cyclic voltammetry did not give firm conclusions for the further reduction stages, except the elimination of one chlorine atom. Thus, the study was continued with constant potential

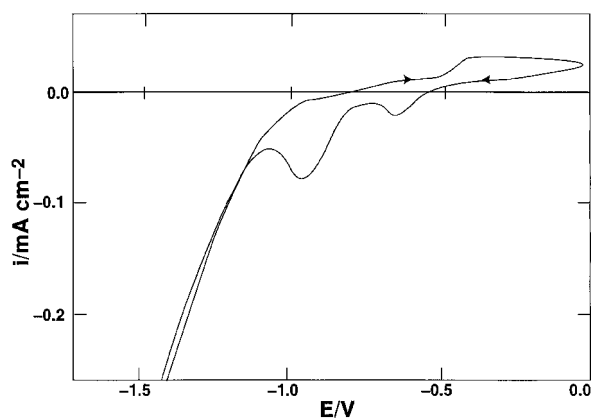


Fig. 4. Cyclic voltammogram of CFC-12 in Bu_4NClO_4 0.1 M on Pb electrode in acetonitrile. Scan rate 100 mV s^{-1} .

electrolytic experiments on silver and lead cathodes. The products detected at Pb (Table 1) were CHClF_2 , CH_2F_2 and CH_3F with current efficiencies (CE) 2.6, 5.5 and 67.1%, respectively. The rate of reduction on Pb was $27 \mu\text{mol s}^{-1} \text{ cm}^{-2}$. This value can be compared to that for other electrodes [6], while on Ag the rate of reduction was significantly higher ($120 \mu\text{mol s}^{-1} \text{ cm}^{-2}$). The main product of the reduction on Pb was CH_3F , which has no particular industrial importance. On Ag CH_2F_2 (39.7%) and $\text{CF}_2=\text{CF}_2$ (30.3%) were produced; these compounds have been used as low temperature refrigerants [3] and as raw materials for polymer production [1], respectively. For these reasons the following experiments were carried out on Ag.

Figure 5 shows the selectivity of the reduction products in relation to the potential applied. The selectivity of each product was calculated as the ratio of its rate of formation to the total rate of reduction. The selectivity of CHClF_2 decreases gradually with increase in the negative potential, whereas the selectivity of CH_3F and CH_4 increases. In addition, the selectivity of CH_2F_2 displays a maximum at -1.25 V . It must be noted that the shape of this curve was similar to that previously reported for basic aqueous solution [8].

Sakellaropoulos [13] proposed a mathematical model for electrochemical reactions of the type $\text{A} \rightarrow \text{B} \rightarrow \text{C}$. The equations derived were applied to experimental results taken from the reduction of fluorocompounds in aqueous solution. The analysis of the results showed that the selectivity of formation of the intermediate product (B) yields at least one maximum depending on the potential, when the number of electrons n_A and n_B , assumed from A and B species, is the same. In the case where $n_A \neq n_B$, more than one maximum can exist. In our experiments the shape of the curves, which appear in Figure 5, for CHClF_2 , CH_2F_2 and CH_4 , exhibit the expected form.

CH_2F_2 shows one single maximum. This is a valid indication that the reactions, which transform CHClF_2 to CH_2F_2 and CH_2F_2 to CH_3F , involve an equal number of electrons. CH_3F , which is an intermediate in the sequence:

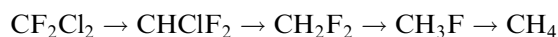


Table 1. Current efficiency of the main products of the electrochemical reduction of CFC-12, at -1.40 V vs SCE, in $(\text{C}_4\text{H}_9)_4\text{NCl}$ 0.1 M at various electrolytes and cathodes

Electrolysis time 3 h

Electrolyte	Cathode	Current efficiency/%					
		CHClF_2	CH_2F_2	CH_3F	CH_4	C_2F_4	Total
CH_3OH	Ag	3.9	58.0	1.8	5.6	0.3	69.6
$\text{CH}_3\text{CH}_2\text{OH}$	Ag	4.2	23.3	5.1	8.6	3.1	44.3
CH_3CN	Ag	0.2	39.7	6.0	1.8	30.3	78.0
DMF	Ag	0.1	6.5	26.1	5.6	3.2	41.5
Propylene carbonate	Ag	6.6	3.3	35.1	12.9	18.5	76.4
CH_3CN	Pb	2.6	5.5	67.1	0.0	0.0	75.2

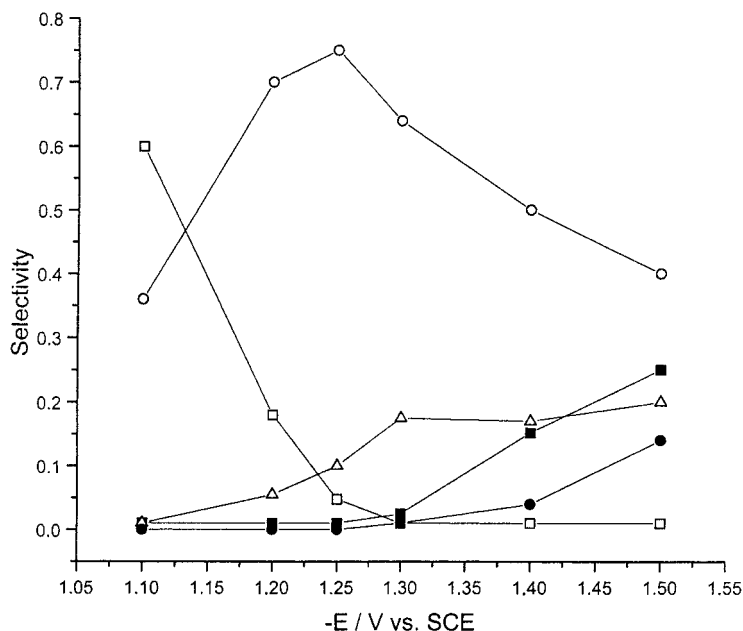


Fig. 5. Selectivity of formation of the reduction products of CFC-12 at a silver electrode, in acetonitrile $(\text{C}_4\text{H}_9)_4\text{NCl}$ 0.1 M medium, against the negative potential, electrolysis time 3 h. Key: (○) CH_2F_2 , (□) CHClF_2 , (■) CH_3F , (●) CH_4 and (△) $\text{CF}_2=\text{CF}_2$.

did not show maxima in the potential region studied. This can be attributed either to side reactions, such as the formation of $\text{CF}_2=\text{CF}_2$, or to the appearance of the maximum at a higher potential. The latter would not be observable, since depletion of the electrolysis medium occurs.

3.2.2. Influence of supporting electrolyte concentration

The effect of the concentration of supporting electrolyte was also examined. It was found that current density increased with increasing supporting electrolyte concen-

tration (Figure 6). When the supporting electrolyte concentration was 0.1 M, the average current density was 45% less than that observed for 1 M concentration. For 0.5 M the current density was found to lie between these values. The total amount of reduced CFC-12 was also increased, hence the total reduction rate in 0.1 M solution was $110 \mu\text{mol s}^{-1} \text{cm}^{-2}$, whereas at 1.0 M it was $190 \mu\text{mol s}^{-1} \text{cm}^{-2}$. Similar behaviour was also observed by Kornienko et al. [14] during the electrochemical reduction of 1,1,2-trichloro- 1,2,2-trifluoroethane, where a gradual shift in the reduction potential to more

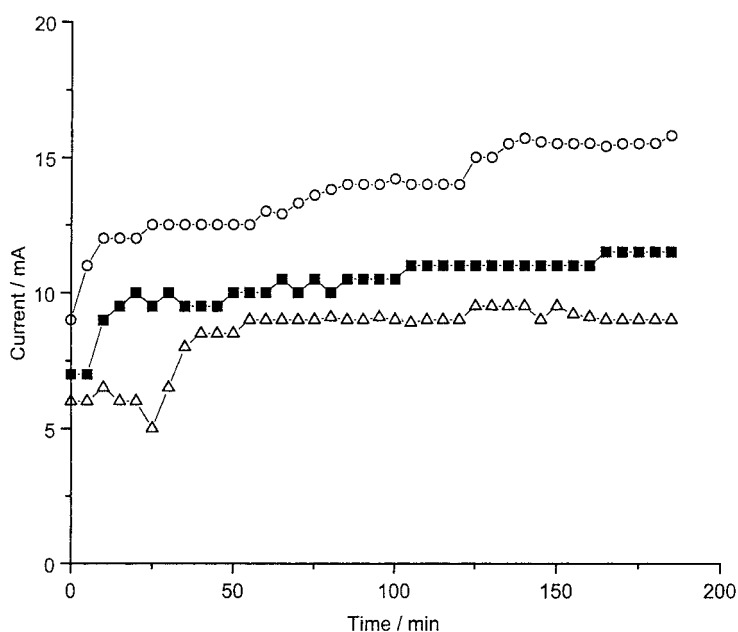


Fig. 6. Total current against time at a the silver electrode, in acetonitrile medium, at potential -1.40 V vs SCE at concentration of $(\text{C}_4\text{H}_9)_4\text{NCl}$. Key: (△) 0.1, (■) 0.5 and (○) 1.0 M.

positive values with increasing supporting electrolyte concentration was observed. This was also apparent in the case of other halogenated compounds and has been attributed [15] to the formation of a positively charged physical complex between $(C_4H_9)_4N^+$ and a halogen derivative that promotes its reduction [16]. Although current density increased with supporting electrolyte concentration, no significant difference was observed on the selectivity of reduction product formation.

3.2.3. Influence of electrolyte

Table 1 shows the current efficiency of the reduction products of CFC-12 in various electrolytes, which contain Bu_4NCl 0.1 M as supporting electrolyte, at -1.40 V. The analysis indicated that the product distribution was strongly dependent on the nature of the electrolyte. In CH_3CN and DMF, only traces of $CHClF_2$ were found. In contrast, $CF_2=CF_2$ was produced in large quantities in CH_3CN and PC. The higher current efficiency for CH_2F_2 (58%) was found in methanol solution.

In addition, a remarkable change in the current density of the reduction products was also observed, as shown in Figure 7. The current density, in most cases, was not stable with time. This is probably due to electrode surface changes, which have also been observed on other cathodes [17]. The average current density was significantly higher in methanol and acetonitrile solutions and much lower in PC (14 times lower than acetonitrile). A significant effect of the nature of the electrolyte on the reduction of the halogen compounds was found by Andrieux et al. [18]. On non catalytic glassy carbon electrodes they observed a significant shift of the reduction potential of $C_6H_{13}I$. They claimed that adsorption is responsible for this behaviour when DMSO was used as solvent. Other

researchers [19] found that the formation of organo-mercury compounds during $C_6H_{13}I$ reduction depends on the solvent and on the supporting electrolyte. The experimental results show that higher current is obtained in acetonitrile, which has lower viscosity (0.345 mPa s). Respectively, the lower current was observed in PC, which has a higher viscosity (2.512 mPa s). It is known that viscosity and diffusion coefficient are inversely proportional quantities. Based on this, the observed differences are attributable to the varying diffusion coefficient of CFC-12 in the various solvents used, although variations in the polarity of the solvent and in the solubility of CFC-12 may also have an important role.

4. Discussion

The more interesting results derived from the reduction of CF_2Cl_2 with cyclic voltammetry and electrolytic experiments are the following. (i) The first stage of the reduction is the receiving of one electron, which results in the elimination of one chlorine atom. (ii) The reduction rate and the distribution of the products are strongly dependent on the nature of the electrolyte and the concentration of the supporting electrolyte. (iii) The selectivity of the formation of the products, with increasing potential showed a decrease for $CHClF_2$, an increase for CH_4 , and a maximum for CH_2F_2 , which assumes that this product is formed with a successive reaction mechanism. (iv) The reduction rate and the products depend on the nature of the cathode. (v) Taking into account the experiments carried out on Pb and Ag in this work and the results of other papers [6–8], the most effective electrode is silver.

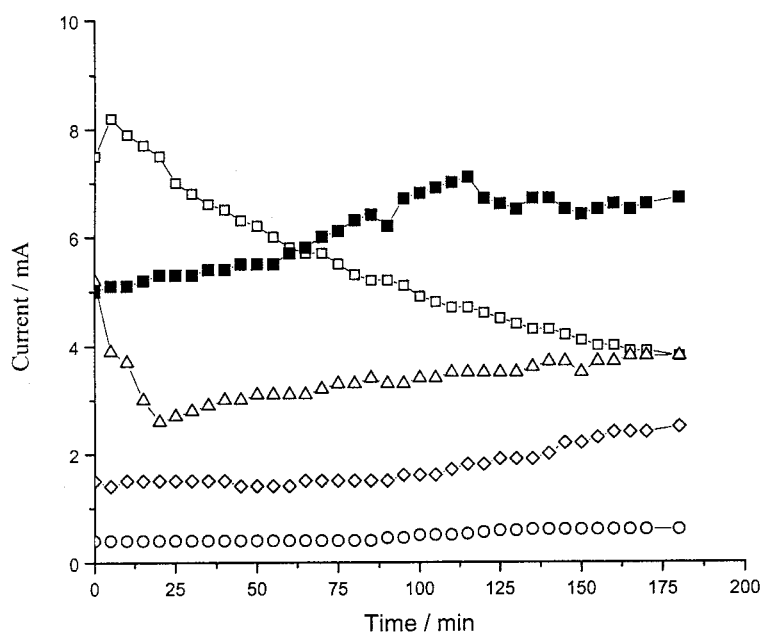
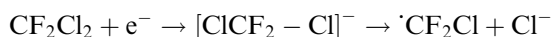
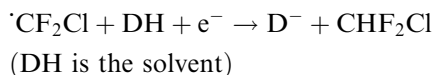


Fig. 7. Total current against time at a the silver electrode, at potential -1.40 V vs SCE, concentration of $(C_4H_9)_4NCl$ 0.1 M in: (■) CH_3CN , (Δ) CH_3OH , (□) CH_3CH_2OH , (◇) DMF, (○) propylene carbonate.

From the above results, the first stage is:



This stage was proposed in other work on the reduction of halogen containing compounds [9, 17, 18]. The radical $\cdot\text{CF}_2\text{Cl}$, receives one hydrogen atom from the solvent and yields CHF_2Cl , which has been detected as a product, according to the following reaction:



CHF_2Cl assumes one electron and takes one hydrogen atom from the solvent yielding CH_2F_2 . The reduction of CH_2F_2 probably continues in a similar way to give CH_3F and CH_4 . This mechanism is similar to the S_N mechanism, which depends strongly on the nature of the solvent, the salts and their concentration, and the pH in the case of aqueous solutions [20].

$\text{CF}_2=\text{CF}_2$, as found in previous work [6], is probably produced by dimerisation of the $\cdot\text{CF}_2\text{Cl}$ and then elimination of two chlorine atoms following the scheme:



In conclusion, the electrochemical reduction of CF_2Cl_2 , is a complex process and further investigation is necessary to clarify the full mechanism.

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